Hydrogenation Mechanism of Coals and Coal Constituents by Structural Analysis of Reaction Products

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Introduction

It is generally conceded that in the hydrogenation reaction of coal the following diversive chemical reactions compete in parallel (among and against each other) as the reaction prodeeds : namely, thermal decomposition, stabilization of active fragments by hydrogen, cleavage of linkage between structural units, dealkylation, dehetro atom, hydrogenation of aromatic ring, ring opening etc. It is also accepted that the various features of these reactions are strongly influenced and change the type of raw coal, their individual chemical structures, properties of the catalyst employed, type of reducing agents, difference in reaction temperature and pressure and the degree of reaction progress. The resulting reaction products are a complex mixture of compounds and because of the fact that the structural analysis thereof is extremely complicated, it follows that elucidation and clarification of the reaction mechanism involved are extremely difficult and the results are far from satisfactory.

Thus we have conducted work on the structural parameters of coal hydrogenation products using the method of Brown-Ladner[1], and from the results obtained we have conducted a follow up on the changes of structural parameters of product accompanying the reaction course; based on the above the outline of the reaction mechanisms have been previously discussed and our results have been reported[2,3]

In the present paper we have selected several kinds of coal samples and using these samples and various reducing agents such as H_2, $H_2 + CH_4$, D_2, D_2 + tetralin, $CO + H_2O$, we have carried out hydrogenation reactions. We have made a follow-up of the structural parameters of the reaction products and we have further discussed the reaction mechanisms involved.

Experimental

The results of the analysis of the sample coal used in the experiment are shown in Table 1. Hydrogenation was couducted using a batch type autoclave with an inner volume of 500 ml. The reaction gas after completion of the reaction was analysed by gas chromatograply. Further, the produced water was quantitated. The whole of the remaining products was quantitated and fractionated by extraction using n-hexan, benzene and pyridine. The fractionation methods are as shown in Table 2, regarding these when fractionation is completed by benzene extraction the conversion was calculated from organic benzene insolubles (O.B.I.) and when fractionation is carried out by pyridine the same was calculated from organic pyridine insolubles (O.P.I.) .

With regards to hydrogenation reducing agents such as H_2, $H_2 + CH_4$, D_2, D_2 + tetralin, $CO + H_2O$ were selected and reduction was conducted by varying the reaction time. Each fractionated fraction was subjected to ultimate analysis, H-NMR, C-13 NMR, molecular weight measurement and the structural parameters were calculated. The results of follow up of these structural parameters in the course of the reactions were considered together and the reaction mechanisms thereof were discussed.
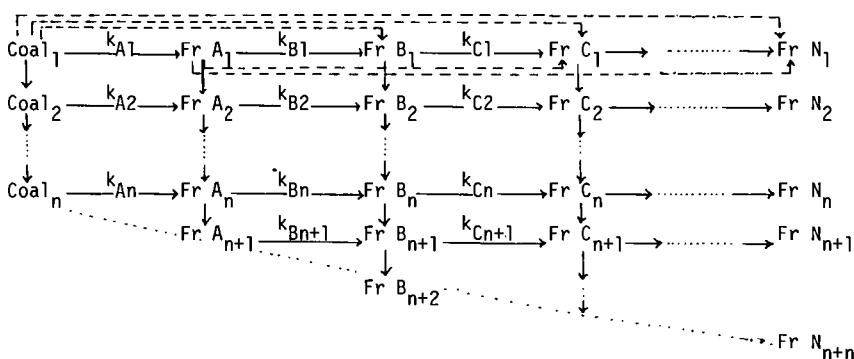
Results and Discussion

Product distribution

Hitherto from a considerable time back high pressure hydrogenation reaction has been dealt with as a consecutive reaction pass through asphaltene as the intermediate[4][5][6]. Further it has been pointed out that Py-1, O_2 likewise shows the behavior of intermediates[3].

In Fig. 1 the following is depicted; the hydrogenation products of Yubari coal at reaction temperature of 400°C were fractionated by the procedure shown in Table 2, and the chagnes of these fraction yield by reaction time are shown. Inasmuch as the presence of Py-2 is scarce in coal, the observed results were obtained in the decreasing period, thus it may readily surmized that an increasing period is present in the initial stage of the reaction. Here we consider oil-1 as the final product, and it may be noted that all fraction other than oil-1, show an initial increase and a subsequent decrease in the course of the reaction and it is clear that they show the behavior of intermediate products in a consecutive reaction. A more or less similar reaction was observed in other reducing agents.

Based on previous work[7][8] regarding the distribution of molecular weight of these fractions, it is known that these have a wide distribution of molecular weight. It is also known that raw coal itself has a structural distribution[9][10]. Therefore it may be considered that in the high pressure hydrogenation of coal, the reactivity of remained unreacted coal is gradually changed and also consecutive degradation of coal is being conducted. This consideration may be expressed in a schematic diagram as follows.

$$
\begin{array}{llllllll}
\text{Coal}_1 & \xrightarrow{k_{A1}} & \text{Fr A}_1 & \xrightarrow{k_{B1}} & \text{Fr B}_1 & \xrightarrow{k_{C1}} & \text{Fr C}_1 \rightarrow & \cdots\cdots \rightarrow \text{Fr N}_1 \\
\text{Coal}_2 & \xrightarrow{k_{A2}} & \text{Fr A}_2 & \xrightarrow{k_{B2}} & \text{Fr B}_2 & \xrightarrow{k_{C2}} & \text{Fr C}_2 \rightarrow & \cdots\cdots \rightarrow \text{Fr N}_2 \\
\text{Coal}_n & \xrightarrow{k_{An}} & \text{Fr A}_n & \xrightarrow{k_{Bn}} & \text{Fr B}_n & \xrightarrow{k_{Cn}} & \text{Fr C}_n \rightarrow & \cdots\cdots \rightarrow \text{Fr N}_n \\
& & \text{Fr A}_{n+1} & \xrightarrow{k_{Bn+1}} & \text{Fr B}_{n+1} & \xrightarrow{k_{Cn+1}} & \text{Fr C}_{n+1} \rightarrow & \cdots\cdots \rightarrow \text{Fr N}_{n+1} \\
& & & & \text{Fr B}_{n+2} & & & \\
& & & & & & & \cdots\rightarrow \text{Fr N}_{n+n}
\end{array}
$$

In other words, coal$_1$ is raw coal, is reacted and lead to a change to a one step lower molecular fraction Fr A$_1$, and at the same time as a side reaction Fr B$_1$ Fr N$_1$ is directly produced. Coal$_2$, the remaining coal from which the above constituents have been lost from coal$_1$, would naturally have a different composition and reactivity of that of coal$_1$. A similar reaction may be expected when Fr A$_1$ undergo a change to Fr B$_1$. The method of dealing with the above indicates the molecular lowering direction of the reaction of hydrogenolysis, and it may be surmized that the chemical reaction of each step would be highly complex.

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Based on the above consideration, the mode of kinetic study carried over a wide range, is solely a means to express how the fraction, fractionated by a certain method, changes quantitatively in the reaction course. In other words these experimetnal results are expressed in equation for convenience dake. And it may be considered that it may considered as a practical means in applicable form.

Now, each respective fraction shows a structural change along with the reaction course, it may be xonsidered at the same time that it contain transfer material from a higher molecular fraction. In other words, for instance Fr A_2 is produced from coal 2 which changes by hydrogenolysis and at the same time, the residue resulting from the reaction from Fr A_1 to Fr B_1 is transferred and exist in a mixed state.

This should be taken in to consideration when the reaction mechanism is to be discussed. In Fig. 1, it may be appropriate to consider that the structural changes of Py-1, Py-2 in the course of the reaction are due to the reaction itself.

Hydrogenolysis by H_2

Hydrogenolysis was conducted using Yubari coal at a reaction temperature of 400°C. The changes of ultimate composition and structural parameters of the Py-1 fraction of the hydrogenolysis products in the reaction course are shown in Fig. 2. Whereas oxygen and sulfur decreases with the prodeeding of the reaction, the nitrogen containing structure is refractory against hydrogenolysis, and a tendency for the nitrogen to be concentrate with the reaction time was recognized. Inspite of the Py-1 in the reaction course yield decrease brought about by hydrogenolysis, however the structural parameters are almost the same which suggests that Yubari coal has a uniform unit structure. The decrease in Hau/Ca in the latter part of the reaction, even when considered together with the behavior of other parameters, it cannot be considered that this is the result of growth of the condensed aramatic ring of Py-1. From the results of an investigation of the structural analysis method using C-13 NMR, in spite of the fact that Hau/Ca should increase when saturation of the aromatic sings arises, because of the Brown-Ladner assumption which has it that diphenyl type linkage is lacking, in contrast cases where Hau/Ca decreases in size may be present[1]. Therefore, it is donbtful the Hau/Ca directly reflects the degree of aromatic ring condensation. From the above in the latter part of the reaction of Py-1, if we could consider that saturation of the aromatic ring has arisen, it may be conceded that an increase in σal (alkyl group substitution) is present. Although it can be stated that by the decrease of the molecular weight, the Py-1 is transfer to asphalten, when the structural parameters of Py-1 and asphalten are compared, it may be conceded that at this molecular weight lowering step deoxygen reaction, depolymerization, ring saturation (side chain substitution -σal') and likewise an increase in side chain substitution over C_2 etc are taking place. Similar results may be observed in the hydrogenolysis of Bayswater vitrinite concentrate, and inertinite concentrate.

Hydrogenation by $H_2 + CH_4$

It was noted that CH_4 is produced as largest gas product in the hydrogenolysis od coal and is found coexisting with resucing hydrogen, the influence thereof on the reaction mechanism was investigated. When methane was added at a pressure of 25 or 50 kg/cm^2 to the initial hydrogen pressure of 75 kg/cm^2 and the hydrogenolysis reaction rate constant was measure. The results are as shown in Table 3.

It may be seen that the reaction rate constant mainly depends on the hydrogen

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partial pressure. However, as compared with the hydrogen only where methane is added at a pressure of 25 kg/cm^2, a slightly higher value is seen. But, in the case of 450°C likewise it may be considered that it solely depends on hydrogen partial pressure. The results of an investigation on the chang of structural parameters of the reaction products by reaction time are shown in Fig. 3. This, it may be considered that the increase in hydrogen pressure mainly enhances the saturation of aromatic rings (as a result an increase in α-hydrogen is seen).

D_2, D_2 + tetralin reduction of coal

In order to clarify the attack site of the hydrogen used for reduction, D_2 was used as the reducing agent and deutrization of coal was conducted and an investigation of the D distribution of reaction products was carried out. For the measuring distribution of D, D-NMR was used, and determination of D divided in 3 categories namely aromatic D(Da), D bonded carbon α from aromatic ring (Dα), D bonded carbon further β from aromatic carbon was conducted. The results are as shown in Table 4. Da, Dα, Do was concerted into H an approximately similar hydrogen type distribution, as seen when H$_2$ was used, was obtained. However, when compared with the distribution of hydrogen remaining in the reaction products, it was shown that a marked maldistribution of diutruim at the α position was seen. It was also noted that when tetraline is used as the vehicle, this tendency because more pronounced.

In addition to the minute amounts of hydrogen in the produced gas, corresponding to the maxiym 34% of hydrogen in coal is present as H-D, and it is known that regarding D in the reaction products, not only D from the reaction but also D arising from the H-D exchange reaction are present. While there is a strong selectivity of H-D exchange reaction[2], the ratio of Da, Do is comparatively high in the products of the initial stage and further even with the increase in reac tion time, since the Da, Dα, Do ratio does not approach the Ha, Hα, Ho ratio, it may be considered that a larger portion of D reacts to α carbon from the aromatic rings.

Reduction by CO + H$_2$O

In Fig. 4 is shown a comparison of changes of the structural parameters of the reaction products in the reaction course where reduction of Soya coal samples is conducted using H$_2$ and CO + H$_2$O. The greatest difference between the two, while it is the same fraction under almost the same conversion, in a CO + H$_2$O system, there is a scarcity of oxygen containing structure. Further when H$_2$ is used, in asphaltene the σal' portion (hydrogen bonded α carbon from aromatic carbon) is smaller as compared with the CO + H$_2$O system. Still further under the present condition the main reaction involved in molecular lowering is depolymerization, so the nacent hydrogen coming form CO + H$_2$O has a selectivity to attack the ether linkage, in addition it may be considered that H$_2$ compared with this, has a definite activity for the cleavage of the CH$_2$ bridge.

Conclusion

The structural parameter changes of products of coal reduction reaction under various reducing reaction conditions were followed up, and a discussion the reaction mechanisms involved was made and the following conclusion were obtained.

1)   It may be considered that in the hydrogenolysis reaction of coal, the coal is subjected to consecutive changes in components and reactivity which results in a consecutive molecular lowering.

2)   Regarding the chemical reaction observed under comparatively mild hydrogenolysis,

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cleavage of linkage between structural units, satruation of aromatic rings, ring opening, dealkylation, deoxygen, desulfurization were seen.

3) When high pressure hydrogen was used as the reducing agent, it could be considered that as a result the addition of hydrogen to α-carbon from the aromatic ring was highest. This was further promoted by increasing the reaction pressure.

4) It may be considered that the nacent hydrogen more selectively contributed to the cleavage of ether bridge and that H_2 was more selective than $CO + H_2O$ regarding the cleavage of the CH_2 bridge.

And also recognized that follow up the changes of structural parameters in the course of reaction is effective to elucidate the reaction mechanism of coal hydrogenolysis.

References

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Table 1   Analytical data on the coals studied

Sample	Proximate analysis %				Ultimate analysis %				
	M.	Ash	V.M.	F.C.	C	H	N	S	O
Soya Koishi [*1]	15.5	15.7	33.6	35.3	73.0	6.6	1.5	0.0_4	20.0
Bayswater Vi [*2]	3.4	1.6	32.9	62.1	83.0	5.3	2.0	0.5	9.2
Bayswater In	4.5	16.2	20.8	58.5	85.0	4.1	1.9	0.3	8.7
Yubari	1.1	6.8	43.6	48.5	85.2	6.2	1.6	0.1	6.9
Shin Yubari	1.2	7.4	34.7	56.7	87.4	6.5	1.8	0.0_4	4.7

[*1]   Austrarian, Vitrinite 99% concentrate
[*2]   "   Inertinite 95% concentrate

Table 2   Fractionation of coal hydrogenation product

Solvent	Fractionation procedure		Fraction	Symbol
N-hexane	1	Room temperature decantation	Oil-1 : n-hexane soluble oil	O_1
	2	Soxhlet extraction	Oil-2 : n-hexane extract	O_2
Benzene	3	Soxhlet extraction	Asphaltene : benzene soluble, n-hexane insolubles	A
			(Organic benzene insolubles)	(O.B.I.)
	4	Room temperature decantation	Pyridine soluble, benzene insolubles	Py-1
Pyridine	5	Soxhlet extraction	Pyridine extract	Py-2
		Soxhlet extraction residue	Organic pyridine insolubles	O.P.I.

Table 3   Reaction rate constant for Shin-Yubari coal hydrogenolysis under different reducing gas composition

Reaction Temp.	Reducing gas composition (kg/cm^2)	Reac6ion rate constant min.$^{-1}$ $k_1 + k_3$	k_1	k_3
400°C	H_2 75	0.0115	0.0037	0.0078
	H_2 75 + CH_4 25	0.0133	0.0050	0.0083
	H_2 75 + CH_4 50	0.0111	0.0033	0.0078
	H_2 75 + Ar 25	0.0109	0.0024	0.0085
450°C	H_2 50 + CH_4 50	0.0178		
	H_2 75 + CH_4 25	0.0230		
	H_2 100	0.0258		

Table 4   H and D distribution of hydrogenation and deutration product of Shin-Yubari coal at 400°C under 50 kg/cm^2 of initial pressure

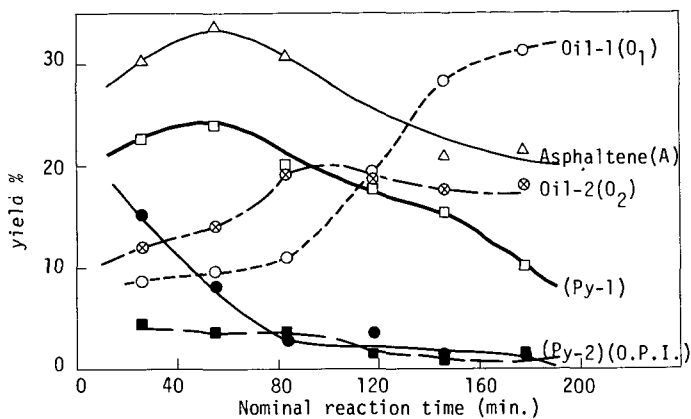| Product	Gas	Rt(min.)	H and D distribution %					
			Ha	Hα	Ho	Da	Dα	Do
Oil	D_2	60	17.5	19.5	63.0	19.4	49.5	31.1
	D_2	120	18.7	21.2	60.1	19.9	50.9	29.2
	H_2	60	21.3	29.6	49.1			
	H_2	120	19.8	31.2	48.9			
	D_{2*}	60	28.8	29.8	41.4	20.1	54.5	25.4
	H_{2*}	60	30.5	35.3	34.2			
Asphaltene	D_2	60	30.3	29.9	39.8	12.9	61.7	25.4
	D_2	120	26.5	29.9	43.5	12.5	55.1	32.4
	H_2	60	27.4	36.4	36.2			
	H_2	120	30.7	34.5	34.8			
	D_{2*}	60	26.1	29.8	44.2	-	68.3	31.7
	H_{2*}	60	29.5	34.2	36.3			

*   with tetraline

Fig. 1   The distribution of products from Yubari coal hydrogenation at 400°C
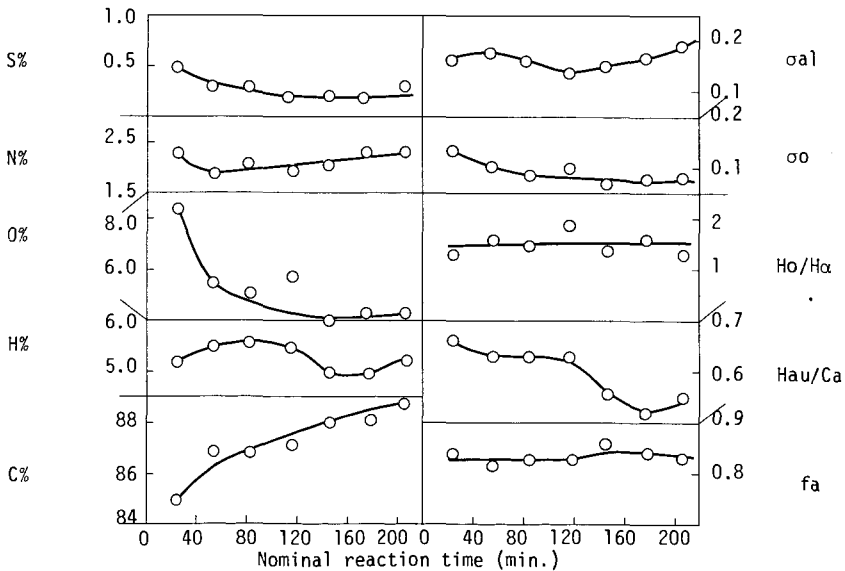

Fig. 2   Ultimate composition and structural parameters of Yubari coal
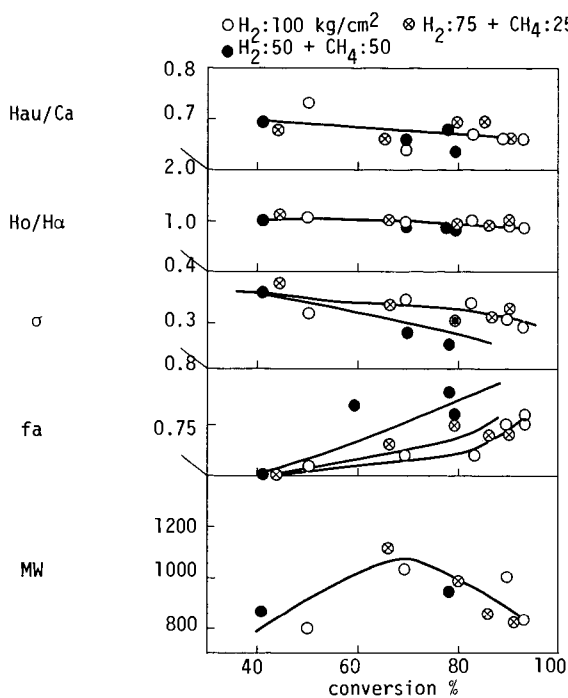hydrogenolysis product Py-1

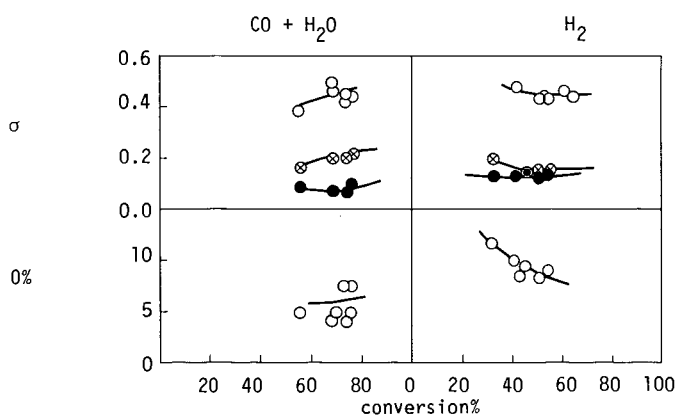Fig. 3　The distribution of structural parameters of asphaltene from Shin-Yubari coal hydrogenation at 450°C

Fig. 4　Structural parameters of asphaltene from Soya Koishi coal by CO + H_2O and H_2 reduction at 400°C